Early Journal Content on JSTOR, Free to Anyone in the World

This article is one of nearly 500,000 scholarly works digitized and made freely available to everyone in the world by JSTOR.

Known as the Early Journal Content, this set of works include research articles, news, letters, and other writings published in more than 200 of the oldest leading academic journals. The works date from the mid-seventeenth to the early twentieth centuries.

We encourage people to read and share the Early Journal Content openly and to tell others that this resource exists. People may post this content online or redistribute in any way for non-commercial purposes.

Read more about Early Journal Content at http://about.jstor.org/participate-jstor/individuals/early-journal-content.

JSTOR is a digital library of academic journals, books, and primary source objects. JSTOR helps people discover, use, and build upon a wide range of content through a powerful research and teaching platform, and preserves this content for future generations. JSTOR is part of ITHAKA, a not-for-profit organization that also includes Ithaka S+R and Portico. For more information about JSTOR, please contact support@jstor.org.

THE POTENTIALS AT THE JUNCTIONS OF SALT SOLUTIONS

By Duncan A. MacInnes

LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF ILLINOIS

Presented to the Academy, August 12, 1915

A concentration-cell consisting of two identical reversible electrodes in contact with two differently concentrated solutions of the same salt gives an electromotive force which is the algebraic sum of three potentials—those at the two electrodes and that at the junction of the solutions. Since for most theoretical purposes the potential at the electrodes alone is desired, many attempts have been made to evaluate the potential at the liquid junction. The effect of interposing strong salt solutions on the electromotive force of the cell has also been studied with the view of eliminating the effect of the liquid junction.

It has been usual to test the correctness of the value assigned to the potential at the junction, or the efficacy of the artifice employed in eliminating it, by seeing whether the resulting electromotive force E at the electrodes can be calculated by the equation $E = (RT/F)\ln(C_1/C_2)$ where C_1 and C_2 are the concentrations of the ions in the two solutions as calculated from conductance measurements, and R, T, and F are the gas-constant, the absolute temperature, and the faraday respectively. Recent work[1] has indicated, however, that the voltages calculated by this formula are too high. It therefore seems desirable to investigate the subject of the liquid junction connecting two solutions of the same salt with a view of finding an expression, involving the fewest possible assumptions, for its electromotice force.

If the cell Ag, AgCl (solid) + KCl (0.1n), AgCl (solid) + KCl (0.01n), Ag operates reversibly until one faraday passes through it, one equivalent of chloride-ion enters the dilute solution and the same amount of chloride-ion is electrolyzed out of the more concentrated solution. The current is carried across the liquid junction by the movement of n_c equivalents of potassium-ion in the direction of the current and by the migration of $(1 - n_c)$ equivalents of chloride-ion in the reverse direction, n_c being the transference-number of the cation. The total effect of the passage of the faraday of electricity is the transference of n_c equivalents of salt, or $2n_c$ equivalents of ion, from the 0.1 normal KCl solution to the 0.01 normal KCl solution. The accompanying electrical work is the product $E\ F$ where E is the total E. M. F. of the cell and F is the value of the faraday. Now the electrical work and consequently the electromotive force at the liquid junction will be determined by the algebraic sum of the number of equivalents of ion that are carried across it from the concentrated to the dilute solution, in this case equal to $n_c - (1 - n_c) = 2n_c - 1$. If we now make the assumption that the osmotic work involved in the transferring of a gram equivalent of positive ion from a dilute to a concentrated solution is the same as the work necessary for the transfer of a corresponding amount of negative ion, we can obtain the electromotive force at the liquid junction by the simple proportion:

$$(E_L F : EF = (2n_c - 1) : 2n_c \quad \text{or} \quad E_L = E\,(1 - 1/2n_c). \qquad (1$$

This equation contains only the directly measurable quantities E and n_c, and contains no assumption concerning the concentrations of the ions in the two solutions.

A direct test of this simple equation is not possible; but an indirect one is afforded by the following considerations. The electrode-potentials of cells of the type Ag, AgCl (solid) + MCl (C_1), AgCl (solid) +MCl (C_2), Ag would be expected to be the same whether hydrogen or any one of the alkali metals is chosen for the radical M, if the concentrations of C_1 and C_2 are the same in each case and below about 0.05 normal. The sum of the electrode-potentials is determined by the difference of the osmotic pressures of the chloride ions in the two solutions; and this difference of osmotic pressure is, probably, nearly the same for dilute solutions of chlorides of univalent cations at corresponding concentrations, since the degrees of dissociation in dilute solution as determined by the conductivity method have been found to be nearly the same for these substances. If this is true, and if the assumption involved in the above-given expression for the potential at the liquid junction is correct, the sum of the electrode-potentials should be independent of the nature of the cation. This amounts to the assumption that the free energy of dilution of the chloride ion is the same whether hydrogen, potassium, or sodium is the cation, since the process at the electrodes during the operation of a cell consists in the formation of one equivalent of chloride ion in the dilute solution and the removal of the same amount of chloride ion from the concentrated solution per faraday passed through the cell. Jahn's accurate work (loc. cit.) on concentration cells with hydrochloric acid, potassium chloride, and sodium chloride is, fortunately, well adapted to test these conclusions.

Table I, which is self explanatory, gives the result of my calculations, based on Jahn's electromotive-force data, which are here given in millivolts. The transference-numbers are from Noyes and Falk's[2] compilation.

TABLE I

Calculation of the Liquid Junction Potential and Electrode Potentials (in Millivolts) of Chloride Concentration Cells With Silver—Silver Chloride Electrodes

SUBSTANCE	MOLS PER LITER	TRANSFERENCE NUMBER	E. M. F. OF CELL E	LIQUID JUNCTION POTENTIAL, E_L	ELECTRODE POTENNTIAL $(E - E_L)$	AVERAGE DEVIATION FROM MEAN
HCl.........	0.01665 0.001665	0.833	−92.35	−36.94	−55.41	0.24
NaCl........	0.01673 0.001674	0.396	−43.60	+11.46	−55.06	
KCl.........	0.01670 0.001674	0.496	−54.24	+00.44	−54.69	
HCl.........	0.03330 0.003329	0.833	−91.62	−36.64	−54.98	0.25
KCl.........	0.03347 0.003347	0.496	−54.03	+0.43	−54.47	
HCl.........	0.008315 0.001665	0.833	−64.87	−25.95	−38.92	0.04
NaCl........	0.008364 0.001674	0.396	−30.73	+ 8.08	−38.81	
KCl.........	0.008329 0.001670	0.495	−38.44	+ 0.39	−38.83	
HCl.........	0.006686 0.001665	0.833	−56.14	−22.45	−33.79	0.08
NaCl........	0.006686 0.001674	0.396	−26.53	+6.97	−33.49	
KCl.........	0.006700 0.001670	0.495	−33.30	+0.34	−33.64	

It will be observed that in each group of cells in which the solutions of electrolytes have the same concentrations, the calculated sum of the electrode-potentials has the same value within a few tenths of a millivolt. This is true even though the liquid-junction potential in the case of the hydrochloric acid cells is 40% of the total electromotive force, and of opposite sign to that in the case of the sodium chloride solutions. The agreement is as close as can be expected from our knowledge of the transference-numbers. Calculations based on other work by the same author show a similar agreement.

This result indicates, at any rate in the case of solutions of concentrations up to 0.03 normal, the correctness of the two assumptions involved in the calculations, namely, that the osmotic work of transferring equivalent quantities of the ions is nearly the same for positive ion and negative ions, and that the osmotic work of transferring chloride-ion from one salt concentration to another is nearly the same whether the cation is potassium, sodium, or hydrogen. It is probable that the first of these assumptions is substantially correct up to much higher concentrations than it can be tested by the method here employed, since this method involves also the second assumption just stated, which doubtless becomes inexact at higher concentrations. Equation (1) here considered must in any case give a much more exact value of the liquid potential than does the Nernst equation

$$E_L = \frac{RT\ (1 - 2n_c)}{F} \ln \frac{C_1}{C_2}.$$

How much the values calculated by the latter differ from those calculated by the former equation in the case of the more concentrated of these dilute solutions is shown in the following table:

SUBSTANCE	MOLS PER LITER	LIQUID POTENTIAL IN MILLIVOLTS		DIFFERENCE
		By equation (1)	By Nernst equation	
HCl	0.01665 0.001665	−36.94	−38.03	1.09
NaCl	0.01673 0.001673	11.46	11.72	0.26
KCl	0.01670 0.001674	00.44	00.45	0.01
HCl	0.03330 0.003329	−36.64	−38.23	1.59
KCl	0.03347 0.003347	0.43	0.45	0.02

The difference between the values for the liquid junction potential as calculated by the two methods is small for salts having ions with nearly the same mobility, but the difference increases rapidly with increased concentrations of the solutions, since the Nernst equation contains the assumption that the ions are 'perfect' solutes, an assumption which is not even approximately true at higher concentrations if the ion concentrations are calculated in the usual manner from conductance measurements.

In conclusion it may be noted that the value of E/n_c in equation (1) when multiplied by F, the value of the faraday, represents the maximum work or free-energy change attending the transfer of one equivalent of salt from one concentration to the other, and that therefore E_L may be calculated from any of the properties related to osmotic pressure, such as freezing-point. This free energy-change may also be obtained directly from electromotive force measurements of cells without transference of the type;Ag, AgCl (solid) + KCl (0.1n), $K(Hg)_x$ – $K(Hg)_x$, AgCl (solid) + KCl (0.01n), Ag, investigated by MacInnes and Parker.

---

[1] See for instance, Jahn, *Zs. physik. Chem.* 33, 545 (1900); Tolman and Ferguson, *J. Amer. Chem. Soc.* 34, 232 (1912); MacInnes and Parker, *J. Amer. Chem. Soc.* 37, 1445 (1915).

[2] *J. Amer. Chem. Soc.* 33, 1454 (1911).

A STATISTICAL STUDY OF THE VISUAL DOUBLE STARS IN THE NORTHERN SKY

By Robert G. Aitken

LICK OBSERVATORY, UNIVERSITY OF CALIFORNIA

Presented to the Academy, August 26, 1915

The double star survey, initiated in April, 1899,[1] has now been completed to –14° Declination for the winter sky and to –22° Declination for the summer sky. This is about as far south as atmospheric conditions make it desirable to extend the survey at Mount Hamilton.

The original plan contemplated the examination with one of the refracting telescopes of the Lick Observatory of all stars as bright as 9.0 magnitude in the *Bonn Durchmusterung*, the identification of all previously known double stars, and the cataloguing of any new pairs, not exceeding 5″.00 in angular separation. Limits must be imposed in work of this character, and those chosen, while necessarily arbitrary, were selected after careful study as being liberal enough for the purpose in mind, which was the accumulation of data for a statistical study of the number and distribution of the visual double stars.

The survey has yielded 4300 new double stars, 1328 discovered by Prof. W. J. Hussey, the others by the writer. Twenty-eight of these have angular separation slightly exceeding 5″.00; 3199, or 74.4% of the whole number, fall within the limit 2″.00, and 1280 (29.8%), within the limit 0″.50. The distance limit adopted has thus been carefully observed, but for various reasons many stars fainter than the limit 9.0 were ex-